Radiation-induced solidification of ionic liquid under extreme electric field

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Abstract
An extreme electric field on the order of $10^{10}$ V m$^{-1}$ was applied to the free surface of an ionic liquid to cause electric-field-induced evaporation of molecular ions from the liquid. The point of ion emission was observed in situ using a TEM. The resulting electrospray emission process was observed to create nanoscale high-aspect-ratio dendritic features that were aligned with the direction of the electric field. Upon removal of the stressing field the features were seen to remain, indicating that the ionic liquid residue was solidified or gelled. Similar electrospray experiments performed in a field-emission scanning electron microscope revealed that the features are created when the high-energy electron beam damages the molecular structure of the ionic liquid. While the electric field does not play a direct role in the fluid modification, the electric stress was critical in detecting the liquid property change. It is only because the electric stress mechanically elongated the fluid during the electrospray process and these obviously non-liquid structures persisted when the field was removed that the damage was evident. This evidence of ionic liquid radiation damage may have significant bearing on electrospray devices where it is possible to produce high-energy secondary electrons through surface impacts of emitted ions downstream of the emitter. Any such impacts that are in close proximity could see reflected secondary electrons impact the emitter causing gelling of the ionic liquid.

Keywords: in situ TEM, in situ FE-SEM, ionic liquid, electrospray, electron radiation

(Some figures may appear in colour only in the online journal)

1. Introduction
Ionic liquids (ILs), or room-temperature molten salts, have low vapor pressures on the order of $10^{-10}$ Pa [1], and thus remain liquid even in a high vacuum environment [2]. In addition, ILs can also have very high electrical conductivity [3]. As such they are used in many applications which take advantage of one or both of these attributes, including wetting agents in high-vacuum electron microscopy studies [4–7], battery electrolytes [8–10], and as propellants for electrospray spacecraft propulsion [11–19]. In spacecraft that utilize IL electrospray, extreme electric fields are applied to the free surface of an IL in order to extract and accelerate ions and/or droplets. The emitted spray produces a reactive thrust which can provide small impulsive thrust to spacecraft.

While electrospray is perhaps best known for its ability to produce fine monodisperse nano-droplet aerosol mists from aqueous solutions, the physics of IL electrospray is somewhat different. Owing to their high conductivities $\sim$1 S m$^{-1}$ [3], ILs form conical menisci (Taylor cones) having an apex radius of curvature approaching a few nanometers. The exceedingly sharp equipotential surface at the apex produces
electric fields estimated to be $10^{10}$ V m$^{-1}$; these extreme fields cause electric-field-induced evaporation wherein liquid-phase ions are extracted directly to the vapor phase [20–23] and no liquid droplets are ejected [12, 24]. The ion current from a single emitter can range from a few nanoamps up to single microamps. Post-test inspection of electrospRAY emission sites has revealed permanent micro-scale damage to both the IL itself as well as the underlying solid substrate (needle) [17, 25–28]. In one particular study completed by Leguinto et al the IL ethylammonium nitrate formed ‘thread like structures’ under application of a strong electric field; these structures spawned multiple current emission sites, which consequently produced further branches to the structures [28]. The structures remained intact after the electric field was removed and thus the IL residue could no longer be considered liquid. They concluded that the phenomenon was likely the result of extremely intense electrostatic fields.

Another unexplored hypothesis for the branched structures is that the molecular integrity of the IL is permanently damaged by impacting high-energy electrons. In the electrospRAY apparatus these electrons can be borne of secondary emission when the electrospayed ions impact solid surfaces downstream of the emitter; these secondary electrons would be attracted back towards the positively biased needle and thus impact the liquid meniscus with high energy [29, 30]. Other environments exist in which high-energy electrons may impact ILs; one of these is in low-Earth and geosynchronous orbits used by spacecraft that use electric propulsion devices [31]; these often use ILs as the propellant [32, 33].

Radiation environments also exist in a laboratory setting, and provide a means to study the effects of electron and gamma radiation on test samples. ILs are used as the solvent for these studies as they can be crafted to accept a myriad of different solutes. Kimura et al used ILs as the solvent for
characterized [34, 35]. Marcinek et al used two ILs in pulse radiolysis to generate radical ions from solutes which could then be characterized [36]. Researchers have also studied the effects that radiation has on the neat ILs. Jagadeeswara Rao et al has shown the viscosity and electrochemical windows of several imidazolium-based ILs are altered when exposed to doses of gamma radiation [37]. Huang et al [38], Shkrob et al [30], and Tarábek et al [39] have shown that irradiation of ILs, either using gamma or electron radiation, yields hydrogen gas, fluorine, and other free radicals depending on the cation and/or anion composition of the IL.

One specific laboratory-based environment that harnesses electron radiation is an electron microscope. As mentioned previously, many ILs have low vapor pressures which are ideal for the vacuum environment of an electron microscope. Furthermore, specific ILs have high conductivities [3], which provide the means to dissipate charge-buildup created by electron beam bombardment [40]. Researchers have found this advantageous when imaging a sample in an electron microscope that must be in a liquid solution [4, 7, 41]. Researchers have also imaged pure ILs using electron microscopy to analyze their molecular cluster structures. Chen et al noted that beam exposure ablated the freestanding liquid, but left the molecular structures [42]. Shirai et al used electron holography to measure the electrostatic potential on the surface of an IL within a transmission electron microscope (TEM) chamber and found that the electron irradiation both changed the liquid to a solid and increased the electrostatic potential at its surface [43]. Such studies indicate that using ILs within high-energy electron environments can change the liquid’s rheology and can affect their use as the working fluid of an experiment. Here, in this study, we use in situ electron microscopy approaches to observe the dendritic growth of IL in real time, and by controlling electron beam exposure we elucidate the debate on the mechanism of structural branching and rheological change during an electrospray process.

2. Methods

The goal of work reported here was to observe in real-time the nanoscale fluid dynamics occurring at the interface of an ionic liquid under extreme electrostatic stress while exposed to an electron radiation environment. To accomplish these goals two electrospray setups were used, one for use in a TEM and one for tests in a field-emission scanning electron microscope (FE-SEM), figure 1.

Experiments were performed in two separate facilities. A JEOL JEM-2100 LaB6 TEM was used to monitor the electrospray during active emission. The TEM is housed in University of Maryland’s Advanced Imaging and Microscopy Laboratory (AIMLab). The TEM was operated at 200 kV to produce images that were digitally captured by a CCD camera. The specimen chamber was kept at a pressure of 10⁻⁶ Torr.

A Hitachi S-4700 FE-SEM was used to evaluate liquid and structural damage due to high electric field alone (no imaging during active electrospray emission). It is housed in Michigan Technological University’s Applied Chemical and Morphological Analysis Laboratory (ACMAL). The electron beam can be accelerated from 5 to 30 keV. The images produced by the microscope are captured via the microscope software with a spatial resolution of up to 1.5 nm. The specimen chamber was kept at a pressure of 10⁻⁶ Torr. In these tests we attempted to use the FE-SEM to image the source while it was emitting spray. Two difficulties were encountered that prevented this: (1) the high electric field created at the spray emitter tip deflected the FE-SEM probe beam electrons (which have much lower energy than the TEM probe beam) causing image distortion that was difficult to correct, and (2) ions emitted during the spray process impact adjacent structures and the secondary electrons ejected from these impacts overwhelmed the imaging beam and rendered the image unreadable.

An electrospray ionization source was fashioned from a solid electrochemically etched needle coated with a thin film of IL. The needle was placed adjacent to a counter electrode held at high voltage to create an extraction electric field at the needle tip. The apparatus was designed to be compatible with a Nanofactory in situ STM–TEM™ holder. The needle was fabricated from a tungsten wire which was electrochemically etched using a 3 M NaOH solution to realize a 1 μm radius tip. A typical needle is shown in figure 2 to illustrate the surface features produced by the etching process.

The etched needle was potted in a brass TEM sample-holder stub using silver epoxy. The brass stub-needle assembly was held in place by interference fit in a brass tube fixed to the stationary side of the sample holder. The junction of the tungsten needle and the face of the brass stub formed an inside corner geometry that acted as a capillary reservoir to hold a small drop of the IL, figure 1(a) and (c). The IL chosen for this experiment was 1-octyl-3-methylimidazolium...
tetrafluoroborate (OMIM-BF$_4$). The counter-electrode for the TEM experiments was a platinum wire turned down to a cone with a sub-100 $\mu$m tip radius, inserted through an aluminum sheet such that it extended about 250 $\mu$m from the surface, seen in figure 1(b); the counter-electrode for the FE-SEM experiments was a blunted screw head, seen in figure 1(d). Electrical circuit diagrams for the TEM setup and the FE-SEM setup are shown in figures 1(b) and (d), respectively.

The overall approach was as follows. An IL electrospray source was mounted in the specimen chamber of an electron microscope. The microscope electron beam was activated so that the electrospray source could be observed in situ while high voltage was applied to the IL and an electrospray beam was being extracted. In this case the liquid was exposed to both extreme electric field and electron beam radiation. Accumulated damage was monitored in real time and also post-test after the electric field was removed and spray ceased. In separate tests with a new electrospray source high voltage was applied to the liquid without energizing the microscope probe beam (extreme electric field but zero electron beam radiation). Electrospray emission was maintained for a period of time and then terminated. The microscope electron beam was then activated and the source was inspected post-emission to evaluate residue or damage attributable to the previously applied extreme electric field alone.

The procedure for the TEM in situ spray visualization was as follows. The counter-electrode was fixed at an extraction distance of 10 $\mu$m from the tip of the needle and the bias of the needle was increased in 50-V steps to a positive 1000 V, or until current was observed on the emitter. The needle bias was increased in 50-V steps to a positive 1000 V. Regions of interest and the corresponding figure numbers are denoted in the image.

3. Results and discussion

The TEM in situ visualization tests revealed changes in the liquid structure that accumulated in time. Dendritic structures very similar to those observed post-test by Lenguito et al [28], were observed to form slowly over a few minutes at several emission sites along the surface of the needle. The branched features were observed while extracting a positive-ion beam (OMIM$^+$) from the needle. The growth-rate during emission was such that it could be seen in real-time, and the branches continued to grow until the electric field was removed. The elongated features were clearly influenced by the electric stress, having their long dimension radially outward from the tip aligned with the intense electric field. The features remained static even after the electric field was removed, indicating that they were no longer liquid but at least viscoelastic and perhaps rigid. TEM images that capture several of the dendritic features are shown in figure 3(a). The
temporal growth of one feature is also illustrated in figure 4 and visualized in Video 1 of the supplementary information. When we changed polarity to extract a negative BF$_4$ electrospray beam similar growths were observed, however, the amorphous/conical shape of the features that formed differed, figure 3(b). Two images captured in situ are shown in figure 5, in which amorphous/conical features formed and emitted; these emission sites eventually solidified as well and persisted after removal of the electric field, figure 3(b). The temporal emission from these conical sites was also recorded in Video 1 of the supplementary information.

As the possibility exists that the electrostatic field intensity had a role in the formation of the solidified features the electric field at the emission sites shown in figures 4 and 5 was estimated using the two-dimensional Laplace’s equation (1)

$$-\nabla^2 \phi = \frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho \frac{\partial \phi}{\partial \rho}) + \frac{1}{\rho^2} \frac{\partial^2 \phi}{\partial \psi^2} = 0,$$

where $\phi$ is the electric potential, $\rho$ is the radial distance, $\psi$ is the azimuthal angle. Solving (1) along the $\psi = 0$ line, with boundary conditions of at $\rho = r$, $\phi = V$ and at $\rho = D$, $\phi = 0$, where $V$ is the applied voltage, $r$ is the radius of the emitter and $D$ is the distance from the emitter apex to the extractor results in a one-dimensional model of the electric field, $\partial \phi / \partial \rho$, shown in (2)

$$\frac{\partial \phi}{\partial \rho} = -\frac{V}{\rho \ln(D/r)}.$$

This gives an estimated local electric field of 10 V nm$^{-1}$ for the feature in figure 4, and 2 V nm$^{-1}$ for the feature in figure 5. An estimate for the electric field was also calculated based on data from the Leguinto et al to be 10–60 V nm$^{-1}$. This magnitude could be larger as the applied voltage used in the estimate was the normal operating voltage of 7.5 kV, whereas Leguinto et al did not report the electric field when they observe the branching effects, only that they deliberately exceeded normal operating parameters.

The images shown in figures 3–5 were obtained while the operating electrospray source was exposed to the 200-keV TEM probe beam. A hypothesis of our study was that the high-energy electron radiation was damaging the molecular bonds and changing the composition of the IL. To explore this hypothesis two tests were performed in the FE-SEM: (1) both negative and positive electrospray beams were extracted from a needle in the FE-SEM specimen chamber while the FE-SEM electron beam was blocked; (2) identical tests were performed in the FE-SEM in which both negative and positive electrospray beams were extracted from a needle while exposed to the 10-keV electron beam. Because of limitations with the FE-SEM technique the liquid could not be observed.
during spray emission, but only pre- and post-emission when the extracting electric field was turned off. Figure 6 shows the respective micrographs of tungsten needles cleaned (no IL) before emission, after an extended period of emission with no beam exposure, and after an identical period of emission performed under a 10-keV electron beam.

Comparing the micrographs in figures 6(a)–(d) illustrates that running an electrospray in the FE-SEM chamber without beam exposure does not produce any solidified features or residue that remains after the electric field is removed. The needle surfaces show no change and it can be concluded that the liquid was undamaged by the intense electric field applied during the electrospray process. When comparing the micrographs presented in figures 6(a) and (b) to those of figures 6(e) and (f), we see formations that persist after spray has been emitted during electron beam exposure. Specifically, there are dendritic features that formed during positive-polarity (OMIM⁺) emission, figure 6(e), and conical features that formed during negative-polarity (BF₄⁻) emission, figure 6(f). Comparing the TEM images in figures 3–5 to
SEM micrographs in figures 6(e) and (f) it was concluded that the high-energy electron environment of the TEM beam caused the features shown in figures 3–5.

We conclude that the solidified or gelled features that persist after removal of the electric field are formed because the high-energy electron beam cross-links or otherwise damages the molecular structure of the IL. The mechanism that may cause this is the cleaving of B–F, C–N, C–H, and/or C–C bonds. As noted earlier, irradiation of ILs can result in high yield of H2, F−, and other radicals which could only come from the dissociation of these atoms from the parent molecule. However, the means to measure the yield of any of these compounds was not available in this study. Therefore, the possibility exists to measure such yields and provide evidence as to which mechanism caused the solidification in a future investigation. We also conclude that while the electric field does not play a direct role in the fluid modification, the electric stress was critical in detecting the liquid property change. A stationary IL that is gelled or damaged by electron irradiation appears visibly unchanged under TEM or FE-SEM imaging when compared to undamaged liquid. It is only because the electric stress mechanically elongated the fluid during the electrospray process and these obviously non-liquid structures persisted when the field was removed that the damage was evident.

4. Conclusions

To summarize, an IL meniscus was exposed to extreme electric field stress within the specimen chambers of both a FE-SEM and TEM. As a result of the stress the liquid emitted current through electric-field-induced evaporation and this emission was observed in situ at the nanoscale. High-aspect-ratio branch-like structures aligned with the local electric field, grew in length over the timescale of a few minutes, and were rigidized by the microscope electron beam. In control experiments the extreme electric field was applied alone without a high-energy electron beam. These control experiments showed no evidence of liquid solidification, hence the conclusion is that electron radiation damaged the molecular structure of the IL and drastically changed its rheology. While 200-keV electrons would have enough energy to break the bonds of the imidazolium and tetrafluoroborate molecules, and may be the cause of the solidification, specific yields of resulting radicals were not measured. This provides motivation for further investigation into the specific mechanism. The evidence of IL radiation damage does raise the question on whether similar effects would be observed in other environments with high-energy electrons, specifically pertaining to spacecraft lifetimes in low-Earth or geosynchronous orbit. While there may be some relevance to these applications, it is important to note that the ionizing damage rate introduced by electron microscopy is highly accelerated relative to typical background levels in these environments.

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Supporting information

Video of temporal growth of dendritic features during OMIM emission, and temporal visualization of emission from conical features during BF4 emission. This material is available free of charge online at iopscience.iop.org.

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